



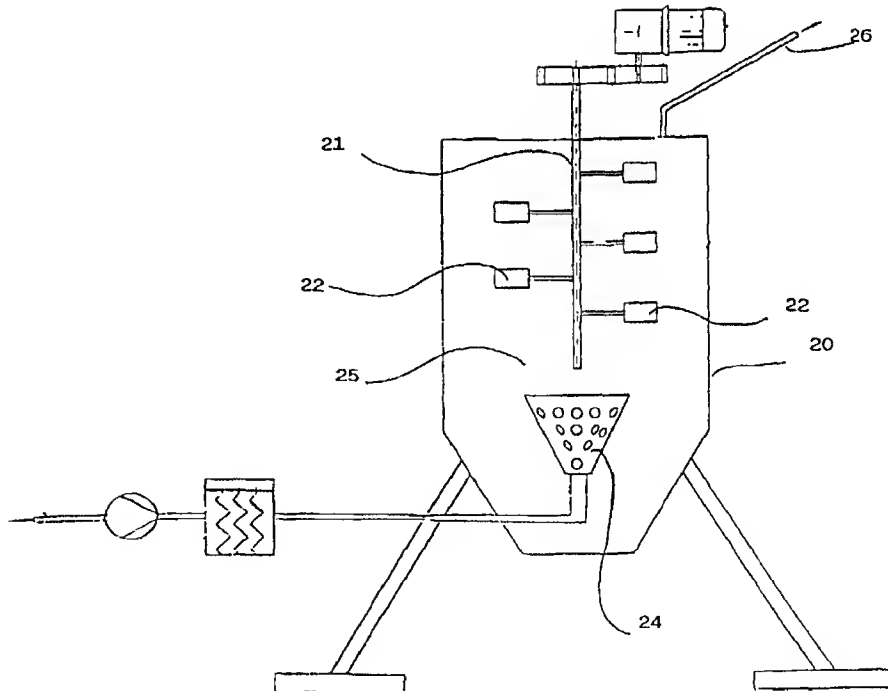
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: METHOD AND APPARATUS FOR THE TREATMENT OF MATERIALS IN THE PRODUCTION OF HOLLOW BODIES OF POLYETHYLENE TEREPHTHALATE

## (57) Abstract

Process pre-treating a mass of thermoplastic resin in its pelletized state, such as P.E.T., which precedes or anyway integrates the drying treatment and consists in maintaining said resin in a flow of inert gas heated to approx. 170 °C for a period of not less than two to three hours, so as to allow said mass of resin to be thoroughly exposed to said flow of inert gas. The purpose of this process is to remove as much free oxygen as possible from said mass of resin, so that the final moulded products obtained from the same resin, i.e. food-grade containers, are almost free from oxygen that might migrate to the food held in the same containers and contaminate it. In a preferred manner, said inert gases are nitrogen or carbon dioxide. The apparatus that carries out this process comprises a container provided with inert-gas blowing means, inert-gas suction means, inert-gas pre-heating means, as well as means for transferring the material from said container to a feeding hopper, under fully sealed conditions with respect to the outside ambient.



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METHOD AND APPARATUS FOR THE TREATMENT OF MATERIALS IN THE PRODUCTION OF HOLLOW BODIES  
OF POLYETHYLENE TEREPHTHALATE

DESCRIPTION

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The present invention refers to an improved method and a related apparatus for the production of hollow bodies of polyethylene terephthalate or P.E.T, or P.E.N., or a mixture of these thermoplastic materials in their pelletized state, of the generally known type used to produce semi-finished products, of the type commonly known as  
20 preforms or parisons, adapted to be subsequently conditioned thermally and blow-moulded for conversion into finished containers, in particular bottles, featuring a very low content of oxygen which might undesirably be released and migrate to, and therefore possibly contaminate, the substances that are subsequently filled into said containers.

25

In particular, the present invention relates to a method and related apparatus for treating said thermoplastic materials, starting from the moment in which they are still in a state of pelletized mass, in order to remove from them the greatest possible amount of oxygen absorbed and present at the moment of the polymerization  
30 thereof.

The process currently used to produce containers of the above cited kind is generally known to be of two basic types, ie. single-stage or two-stage.

Although the characteristics of and differences between said two types of processes are generally known in the art, they will anyway be shortly reviewed below, particularly in order to put the emphasis on the differences in their basic behaviour patterns with particular reference to the effects thereof on the variation in the oxygen content of the final container, which is actually the subject of the present invention.

#### Short review of relevant features of blow-moulding processes

The raw material used in both single-stage and two-stage processes is partially crystalline PET, with a crystallinity of mass-50%. The material is available in pelletized form, typically with a grain size of just a few millimeters, and comes from a storage facility where it is generally kept under ambient temperature and pressure conditions in atmospheric air. Before being sent to extrusion, the pelletized material is dried in an air current at atmospheric pressure and a temperature of 150°C, for a length of time of approx. 5 hours. As a result, when it leaves the dryer, the PET has still a crystallinity of approx. 50% and an oxygen content which, as this will be indicated further on in this description, turns out to be drastically reduced and close to the equilibrium or steady-state one with air at 1 bar and 150°C.

#### Two-stage process

Two-stage processes consist of two subsequent processing steps, the first one of which produces the so-called preforms, or parisons, while the second one then produces the bottles or containers in their final form and aspect.

The first stage starts with the extrusion of the material, in which a working temperature of 280° is usually found to prevail in the extruder screw, along with relatively modest pressures. The overall dwelling time of the PET in the extruder is approx. 5 minutes.

In this phase, the PET remains substantially in contact with air in the feeding hopper, where the temperature is approximately the material temperature when it leaves the drier, ie. approx. 150°C, and the pressure is the atmospheric one. In the screw, during both the melting and the actual extrusion phases, there is no contact

with air, so that these phases have no relevance as far as the variation in the oxygen content is concerned.

5 The PET leaving the extruder is then conveyed to the moulds for the production of the preforms by means of an injection moulding operation. The latter takes place at a temperature of approx. 110°C for a duration of approx. 11 seconds.

10 In the so produced preform, the neck of the bottle is already formed in its final shape, ie. is already capable of ensuring the tight sealing function it is intended to after the resulting bottle has been filled. The remaining body of the preform must on the contrary be subsequently allowed to undergo a blow-moulding operation in view of being converted in a bottle in the final form and aspect thereof. The kinetics of the process is such as to produce preforms of PET material which is completely amorphous, as this is on the other hand required in view of the subsequent  
15 processability thereof and the required transparency of the finished bottle.

The preform constitutes the product that is obtained in the first stage of the process. Before being sent to further processing, the preforms so obtained in the first stage are then stored in contact with atmospheric air and kept in such storage  
20 conditions for even quite long periods of time.

The second stage of the process is then carried out to the purpose of obtaining the finished bottles starting from the preforms. These preforms come from the storage facility and are therefore in a state of equilibrium with the ambient air; in  
25 particular, the oxygen content is the equilibrium one with a partial O<sub>2</sub> of 0.21 bar. They are pre-heated to 100°C and conditioned to such a temperature by means of IR radiation, in appropriate heating stations, again in the presence of ambient air. This phase has an overall duration of approx. 25 seconds.

30 After this phase, the preforms are then transferred to the contiguous blow-moulding tools in which, by means of an appropriate rod being lowered, they are conferred an axial stretching and, by means of air being appropriately blown, the PET material constituting the bottle is conferred a circumferential stretching. In this

phase, the average temperature is 70°C and the wall thickness of the part being processed decreases considerably. During blow moulding, and the resulting biaxial stretching, the material undergoes a partial crystallization of approx. 35%. The overall duration of the blow-moulding step is approx. 7 seconds, of which 0.5 s are spent in contact with primary air at 10 bar, and 1.5 s are spent for blowing with secondary air at 38 bar; in the remaining time, the PET material is in contact with air at atmospheric pressure.

#### Single-stage process

In this kind of process, the production of the preform takes place by first extruding and then injection-moulding the PET material, following the same procedure as used in the previously described two-stage method. The basic difference from the latter lies here in the fact that the so obtained preforms are not cooled and then sent to storage, but are on the contrary exposed immediately to further processing in view of being sent directly to the subsequent conversion phase on the blow-moulding line.

Preforms that leave the injection-moulding stage are at a temperature of approx. 110°C and are conditioned at a temperature of 100°C for approx. 21 seconds. They are then conveyed to the blow-moulding tools, where they undergo the same processing conditions as described previously for the two-stage process.

#### Identification of salient phases as far as oxygen exchanges are concerned

The two above cited kinds of processes are characterized in that they include a number of different phases, in which the material is exposed to atmospheric air at different temperatures for different lengths of time. As a result, the content of oxygen dissolved in the walls of the resulting bottles will be different for the two processes.

To the purpose of providing a comparative assessment of the two different oxygen contents resulting in the PET material from the two processes, the salient phases are considered in which oxygen exchanges take place successively.

Since the dimensions and, in particular, the thicknesses involved are of great importance for the rate of exchange of the oxygen by diffusion, reference is made to

the typical dimensions of a bottle having a volume of 0.500 litres and a mass of 25 gr. Correspondingly, the thickness of the walls in the preform is 3.4 mm, whereas the final bottle has a wall thickness of approx. 0.3 mm.

5       Two-stage process

In this process, the preforms of amorphous PET obtained in the first stage thereof are stored in atmospheric air for an undetermined and generally very long period of time. As a result, at the beginning of the second stage of the process they are provided with an oxygen content that is equal to the equilibrium one for the  
10       amorphous material in atmospheric air at ambient temperature, ie. approx. 25°C on an average.

Under such an initial condition they are then exposed to air at 100°C for 25 seconds during the heating/conditioning phase; in this phase, the wall thickness is  
15       the one of the original preform, less an amount due to the effect of a possible heat expansion. Since oxygen solubility decreases with an increasing temperature, in this phase the material will tend to release part of the oxygen contained initially.

As indicated earlier in this description, in the subsequent blow-moulding phase,  
20       which takes place at an average temperature of 70°C, the preform is stretched and blown under exposure to primary air at a pressure of 10 bar for approx. 0.5 seconds, and secondary air at a pressure of 38 bar for approx. 1.5 seconds. In this process, the wall thickness undergoes a significant reduction and, at the same time, a partial crystallization.

25       In this particular stage of the process, the phase that most of all contributes to the variation in the oxygen contained in the bottle is the stretching action induced by the secondary air. Such an action takes place by exerting a considerably greater pressure upon a larger exposed surface for a longer length of time than typically  
30       experienced with the action brought about by the primary air.

For this reason, the mass contribution of oxygen absorbed in the bottle in this stage of the process is estimated by considering the exposure of the inner surface of

the bottle, in the final dimensions thereof, to a phase of air at 38 bar for a time of 1.5 seconds.

- Conclusively, to the purpose of assessing the most significant oxygen exchanges taking place in the process, the latter can be schematically broken down into following phases, for each one of them the main characteristics are indicated below:

Phase		Initial condition	Temperature (°C)	Duration (s)	Average thickness (mm)	Pressure (bar)	Crystallinity (%)
1	Feeding of preforms	Saturated with air at 1 bar and 25°C			3.4		0
2	Heating/Conditioning	Saturated with air at 1 bar and 25°C	100	25	3.4	1	0
3a	Blow mould. (high P)	As arriving from heating phase	70	1.5	0.3	38	35
3b	Blow mould. (atmosph. P)		70	5.5	0.3	1	35
4	Coating	As arriving from blow moulding	30	5	0.3	1	35

#### Single-stage process

- 10 This process certainly required a closer, more detailed analysis in this connection, since the process itself is actually fed with pelletized material having a 50% of crystallinity and coming from storage and, therefore, saturated with respect to the atmospheric air. The salient phases to be considered here are:

- 15 1) drying for 5 hours in air at 150°C of a pellet having an edge of a few millimetres; conservatively, the pellet is considered as having an edge of 3 mm, although it



usually has a smaller grain size;

- 2) extrusion at 280°C for 5 minutes; as already discussed earlier in this description, this phase has no practical relevance as far as oxygen exchange is concerned, since a contact with air takes only place during the short period of time spent in the feeding hopper, and this actually has only minor, even negligible effects as compared with the ones connected to the preceding drying phase;
- 3) injection moulding of the preforms at 110°C for 11 seconds, with a cross-section size, or wall-thickness, of 3.4 mm; in this phase, the surface that is exposed to atmospheric air is limited to the one of the flow front of the molten polymer moving forwards into the mould; such a surface is negligible if compared with the total surface area of the preform, and it is anyway exposed to air at atmospheric pressure and not at any higher pressure; even in this phase the exchanged mass of oxygen is negligible;
- 4) thermal conditioning for 21 seconds at 100°C in air at 1 bar;
- 5) blow moulding at 70°C with air blown at pressures of up to 38 bar; as indicated earlier in this description, the preform is stretched and blown under exposure to primary air at 10 bar for approx. 0.5 seconds, and secondary air at 38 bar for approx. 1.5 seconds. In this process, the wall thickness undergoes a significant reduction and, at the same time, a partial crystallization. To the purpose of calculating the oxygen that is exchanged with the air by the bottle, it is reasonable to assume that the latter essentially absorbs oxygen in the blow moulding phase with air at 38 bar for a duration of 1.5 seconds. The action of the air is exerted on the bottle in the by now ultimate form and shape thereof, therefore with a wall thickness amounting to 0.3 mm. The surface of the bottle that is exposed to the action of the air at 38 bar is solely the inner one.

Conclusively, to the purpose of assessing the most significant oxygen exchanges taking place in the single-stage process, the latter can be schematically broken down into following phases, for each one of them the main characteristics are

indicated below:

Phase		Initial condition	Temperature (°C)	Duration (s)	Average thickness (mm)	Pressure (bar)	Crystallinity (%)
0	Feeding of pellets	Saturated with air at 1 bar and 25°C			3		50
1	Drying	Pellets	150	18000	3	1	50
2	Extrusion	As arriving from dryer	280	300			0
3	Moulding of preforms	As arriving from extruder	110	11	3.4	1	0
4	Heating/conditioning	Saturated with air at 1 bar and 25°C	100	25	3.4	1	0
5a	Blow mould. (high P)	As arriving from heating phase	70	1.5	0.3	38	35
5b	Blow mould. (atmosph. P)	heating phase	70	5.5	0.3	1	35
6	Coating	As arriving from blow moulding	30	5	0.3	1	35

- 5 Mass of oxygen exchanged in each processing phase and mass of oxygen contained at the end of each phase

In consideration of the schematizations that have been used for the geometry of the matrix, the initial conditions and the ambient and general conditions prevailing in the two types of processes considered (Tables 1 and 2 above), the mass of oxygen exchanged in each single phase of said processes can now be assessed. The mass of oxygen contained in the PET matrix can be calculated from a simple material balance:

$$M_{final} = M_{initial} + M_{exchanged}$$

Oxygen contents have been therefore found out with this procedure. Owing to the calculation procedure being quite long and complex to explain in full detail, this will be omitted here for reasons of greater simplicity and brevity. Anyway, the results obtained for the oxygen content in the PET material at the end of the single phases included in both single-stage and two-stage processes are indicated in Tables 3 and 4, respectively (in mass ppm). For a more complete analysis, also the period of time spent by the just produced bottles in contact with the ambient atmosphere during the phase in which they are collected as they leave the moulding plant has been considered in the calculations, although such a phase is generally known for anyway having an altogether negligible effect in this connection.

Table 3: Oxygen content at the end of the most critical phases of the two-stage process

	Temperature	Crystallinity	Pressure	Characteristic length	O <sub>2</sub> equilibrium content	O <sub>2</sub> content
	(°C)	(%)	(bar)	(mm)	(ppm)	(ppm)
PREFORM FEED	25	0				22.5
CONDITIONING	100	0	1	3.4	8.92	22.3
BLOW MOULD a)	70	35	38	0.3	286	24.6
BLOW MOULD b)	70	35	1	0.3	7.53	24.1
COATING	30	35	1	0.3	14.87	24.0
EXIT	30	35	1	0.3	14.87	23.8

Table 4: Oxygen content at the end of the most critical phases of the single-stage process

5

	Temperature	Crystallinity	Pressure	Characteristic length	O <sub>2</sub> equilibrium content	O <sub>2</sub> content
	(°C)	(%)	(bar)	(mm)	(ppm)	(ppm)
FEED	25	50	1			13.8
DRYER	150	50	1	3	6.02	6.03
CONDITIONING	100	0	1	3.4	8.92	6.03
BLOW MOULD a)	70	35	38	0.3	286	860
BLOW MOULD b)		35	1	0.3	7.53	8.56
COATING	3	35	1	0.3	14.87	8.63
EXIT	30	35	1	0.3	14.87	8.71

As it can be noticed, the two-stage process produces bottles with a capacity of 0.500 litres and a mass of 25 g, with an oxygen content that is estimated to amount to 23.8 ppm, whereas the single-stage process produces the same bottles with an oxygen content that is estimated to amount to 8.7 ppm, ie. an oxygen content that is lower by as much as a factor 2.7 than the one resulting from the two-stage process. With reference to the stated aim of limiting the final oxygen content in the PET material, such a ratio represents a good measure of the advantageousness of the single-stage process as compared to the two-stage one.

15

It is interesting to notice that, when the mass of oxygen contained in the PET is transferred to the liquid contained in the bottle, the oxygen content in the liquid undergoes an increase by 1.2 ppm when bottles produced with a two-stage process are used, whereas such an increase amounts to just 0.44 ppm when use is made of bottles out of a single-stage process.

20

From the results that have been obtained it is possible to infer that, with the usual operating times and conditions recurring in the afore considered processes, the amount of oxygen contained in the walls of the bottles is substantially affected by the actual oxygen content in the PET material being fed to the plant producing the same bottles. In particular, the value that is obtained in the two-stage process is practically dictated by the O<sub>2</sub> content in the preforms that arrive from storage, whereas in single-stage processes such a value is on the contrary controlled by the oxygen content in the pellets that are fed to the extruder and come from the drier.

10

As discussed earlier in this description, the assessment of the oxygen content in the preforms that are fed to the two-stage process is made on the basis of values of the coefficient of solubility that do not take into account the rapid cool-down phase provided for obtaining the same preforms, so that they shall for sure be considered as being underestimated to a significant extent. Therefore, the value 2.7 assigned to the afore cited factor of comparison must correspondingly be regarded as constituting a lower limit, since the actual value of such a factor is most probably much higher than that.

An analysis of the afore indicated results and values shows that, if the oxygen content in the PET material of the bottles has to be lowered, the need first of all arises for the oxygen content in the PET material fed to the production plant to be substantially reduced. Now, this does not appear as being capable of being easily carried out and obtained in a two-stage process, since it does not seem a proposable option for the preforms to be kept in a storage facility with an oxygen-free atmosphere. Quite on the contrary, such an aim seems much more easily pursuable in the case of single-stage processes, in which the pellets are anyway dried for a period of approx. 5 hours immediately before being fed to the extruder.

In fact, prior-art solutions, in connection with which following patents are cited by mere way of example:

- |                |                |                |
|----------------|----------------|----------------|
| - US 4,820,463 | - US 3,862,284 | - US 4,820,463 |
| - US 4,764,405 | - US 5,244,615 | - US 4,880,675 |

- US 5,401,451      - US 5,213,734      - GB 2 053 775

5 teach that barrier properties of the container can be enhanced, and the extent or amount of oxygen absorbed by it can be reduced, by means of treatments that must be carried out substantially on the preform when the latter has already been moulded and finished, in particular immediately before and during the blow-moulding phase.

10 However, all these solutions share a common drawback in that they are strongly conditioned, ie. affected by both the limited effectiveness of the results obtained and the complexity of the processes and the plants involved, which further contributes to the high costs and, eventually, the poor attractiveness of the same solutions.

15 It is therefore a main purpose of the present invention to provide a method and an apparatus that are capable of treating these thermoplastic materials in such a manner as to remove from them a significant amount of the oxygen absorbed by them before being melted and compacted, in a simple, reliable and safe manner and with the use of readily available techniques.

20 Such main aim of the present invention, along with further features thereof, are reached in a method and an apparatus that are made and operate as recited in the appended claims.

25 The features and advantages of the present invention will anyway be more readily understood from the description that is given below by way of non-limiting example, which may be therefore be the subject of a number of variants and modifications, with reference to the accompanying drawings, in which:

30 - Figure 1 is a symbolical, block-diagram view of a single-stage plant according to the prior art;

- Figure 2 is a view of the same plant to which an apparatus according to the present invention, represented symbolically, has however been added;

- Figure 3 is a view of a preferred, basic configuration of a portion of the apparatus indicated in Figure 2;

5       - Figure 4 is a view of the same apparatus shown in Figure 2, in a preferred embodiment thereof, as associated to a feeding hopper of a single-stage or a two-stage plant.

10       If reference is made to Figure 1, this is shown to schematically illustrate a single-stage plant for the production of plastic bottles, according to the general state of the art. This plant can be noticed to essentially consists of a hopper 1, in which the thermoplastic material is introduced in its pelletized state, an extruder 2, in which said thermoplastic material is melted and extruded into a plurality of multi-cavity moulds 3 in view of obtaining from these a sequence of preforms. These preforms are then removed from said moulds and introduced, by means of appropriate handling means, and usually by passing through appropriate temperature conditioning and levelling-off stations 4, in respective blow-moulding tools 5 in which said preforms are therefore blow moulded and converted into the desired final product.

20       These types of plants, as well as the processes that are typically carried out in them, are largely known in the art, so that no need arises here to dwell upon them any longer.

25       The present invention applies to both single-stage and two-stage processes, wherein it shall be appreciated that, in the case of two-stage processes, it only applies to that part of the process which starts with the filling of the thermoplastic material in its pelletized state in the feeding hopper and ends with the removal of the preforms from the injection-moulding moulds.

30       It will on the other hand be also appreciated that the greatest advantage is obtained with the application of the present invention to single-stage processes and plants, although no actual prejudice seems to exist that might impair or even talk against an application to two-stage processes and plants.

According to the present invention, the mass of pelletized PET to be treated is initially introduced in a container into which a current of gas, which will be defined as inert in the following description, thereby meaning any type of gas that would not  
5 bind or combine chemically with said thermoplastic material, is insufflated through appropriately arranged injectors, nozzles or grilles.

It has in fact been found experimentally that ventilating a mass of pelletized thermoplastic material for a certain period of time has the property of absorbing  
10 and/or promoting the removal of the free oxygen being contained in said material.

In this way, when said material is filled in the hopper for being extruded, its content of free oxygen is already drastically reduced, so that the same material is inherently adapted to be converted first into preforms and then into finished blow-  
15 moulded containers that are in practice almost totally free of oxygen and, therefore, will not release any appreciable amount of oxygen into the foodstuffs that are eventually filled in said containers.

During the experimentation and assessment of the characteristics of the process  
20 used to insufflate said stream of inert gas against and through said pelletized thermoplastic material, it has been observed that such a process may be carried out according to various modes of implementation and under various operating conditions tending to improve and/or optimize the final results.

25 The first one of these operating conditions relates to the temperature of said inert gas, which should be pre-heated to a temperature ranging from 120°C and 180°C before being blown into the container in which the mass of pelletized thermoplastic material to be treated has been collected. It has been furthermore been observed that the above cited oxygen-removing process produces an additional advantage  
30 during stretching: it in fact contributes to a reduction in the moisture content in the PET pellets and this, as anyone skilled in the art generally knows very well, proves to be a considerable advantage, since the lower moisture content induced in the pelletized thermoplastic material favours actually the crystallization process in the



surface portion of the preform during blow moulding, owing to the fact that the moisture that is present in the material actually acts as a lubricant to promote the reassembling of the molecules, thereby reducing molecular friction between them and, therefore, reducing also the heat generated by said friction, and ultimately  
5 lowering the extent of crystallization of the bottle.

It is therefore an obvious conclusion that the method according to the present invention for the removal of free oxygen from the mass of thermoplastic material ideally combines into the known process used to remove the moisture from the  
10 same material before extrusion by means of an appropriately heated-up flow of gas blown therethrough for such a long time as required to obtain the desired degree of dryness.

The second condition relates to the actual flow rate of the inert gas and the  
15 duration of the treatment. It has been found experimentally that optimum results are generally obtained when inert gas is insufflated at a specific flow rate (in relation to the weight of the material) of  $0.5 \text{ m}^3/\text{hr.kg}$  for an accordingly shorter duration of two hours.

Those skilled in the art will at this point be fully capable of appreciating that  
20 similar results can be obtained by suitably combining intermediate values of such parameters, although still acceptable results may be reached under extreme conditions at the boundaries of the above cited ones.

The third conditions relates to the nature of the inert gas used to the purpose. It  
25 has of course been verified that nitrogen serves very well the purpose. However, also carbon dioxide may be used effectively, without any significant contraindications, as a further gas that neither binds or combines with oxygen nor interacts with the thermoplastic material under the particular treatment conditions.

30 The fourth condition consists in providing for said mass of thermoplastic material to be suitably stirred as it is being exposed to such a flow of inert gas, so as to improve both the uniformity of the passage of the inert gas over almost the totality of

the surface of the pelletized material, and the condition according to which the temperature of said inert gas, when the same invests the material, must be as uniform and constant as possible. In fact, if the opening through which the gas is insufflated in the container is situated on a side of said container, while the gas exhaust opening is of course situated on the opposite side thereof, as this is quite frequently the case, it ensues that the mass of material near the gas exhaust opening is invested by the flow of inert gas after the same has flown through the greatest bulk of the remaining mass of material and, therefore, has cooled down accordingly. The result is that said mass near the gas exhaust opening is heated up to a lower level than the required one, which thing practically means that both oxygen and moisture removal effects are lowered.

As far as the apparatus for carrying out the above described method is concerned, reference should be made to Figures 2 and 3, which illustrate a container provided with an internal rotating shaft 21 on which there are applied, by means of appropriate arms, a plurality of stirring paddles 22, in which said rotating shaft is driven by per se known means.

However, any other means for stirring the pelletized contents of the container may prove adequate, provided that it is actually capable of ensuring a continuous, uniform stirring of the material.

In an appropriate zone in the interior of the container there is provided an inert gas diffuser 24, which diffuses into the mass of pelletized material a stream of inert gas blown by per se known means (not shown) and appropriately heated up. The container is also provided with an opening 26 through which the inert gas is exhausted upon its having so treated said pelletized material, wherein said inert gas may of course be recovered at the exhaust in view of being regenerated and reused.

Furthermore, in view of an improved efficiency and production continuity, there is provided an extruder feeding hopper 27, which is in turn connected, via an appropriate conduit 28, to said container 20 in which the process according to the

present invention is carried out and which is adapted and controlled so as to cause the therein contained pelletized material to be discharged, after the treatment, into said hopper. To the purpose of preventing any possible contacts with the atmosphere, and therefore any possible contaminations with the oxygen contained in  
5 said atmosphere, both said hopper and said conduit 28 have a sealed, airtight construction.

Figure 4 illustrates an improved embodiment of the present invention, in which the hopper and the container where the pre-heated inert gas is diffused are made  
10 and arranged so as to build a single body 30.

The operation of the apparatus can at this point be quite easily inferred: the container 20 is filled with the mass of PET pellets and the immission of heated inert gas is then activated at the same time with, possibly, the rotation of the paddles for  
15 stirring said mass of pelletized material.

Such an operating condition is maintained for a period of at least two hours, during which the material undergoes a progressive transformation that leads it to assume the afore mentioned and defined properties of dryness and quasi-absence of  
20 oxygen. It will be appreciated that such an insufflation of inert gas into the mass of thermoplastic material while the latter is being stirred in view of preventing it from agglomerating may be implemented with any other means suiting the purpose. For instance, use can be made of a rotating container, of the type similar to the mortar or cement mixing machines and industrial machines used to mix the most varied  
25 substances, provided with internal ribs attached to the inner wall of the container for ensuring the mixing or stirring action, while the inert gas diffuser may be implemented so as to be able to be introduced and removed upon appropriate command through the filling mouth of the mixer-like container. A further option may be a container arranged to rotate about a horizontal axis and provided with two  
30 mouths or openings situated in mutually opposed positions in order to enable the inert gas to be blown therein and exhausted therefrom, respectively.

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CLAIMS

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1. Method for the neutralization of a mass of resin, PET (polyethylene terephthalate), PEN or other blended thermoplastic materials in a pelletized form, characterized in that said mass of resin in a pelletized form is filled in a container in which a flow of inert gas is forcedly blown so as to enable said inert gas to substantially invest the whole mass of said pelletized material by penetrating the interstices thereof.

2. Method according to claim 1, characterized in that said inert gas is pre-heated to a temperature ranging from 120°C to 180°C.

20

3. Method according to claim 2, characterized in that the flow rate of said inert gas is comprised between 0.5 m<sup>3</sup>/hr.kg and 5 m<sup>3</sup>/hr.kg of pelletized material in its original state, and that the duration of said drying and neutralizing treatment is comprised between 2 and 10 hours.

25

4. Method according to any of the preceding claims, characterized in that said inert gas is nitrogen or carbon dioxide.

5. Method for the production of hollow bodies of thermoplastic material, comprising the phases in which a mass of thermoplastic material is melted and is then extruded into a plurality of intermediate products, as well as a phase in which said intermediate products are blow moulded for conversion into the desired finished products, characterized in that it further comprises a neutralization phase

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carried out with inert gas in accordance with any of the preceding claims or any combination thereof, and that this neutralization phase is carried out immediately before said phases in which said thermoplastic material is melted and extruded.

5        6. Apparatus for the production of hollow bodies out of a thermoplastic material which is fed in its pelletized state to the same apparatus, characterized in that it comprises a container (20) along with

- means for continuously stirring and mixing said pelletized thermoplastic material,

10       - and means for blowing in and circulating a continuous flow of inert gas in said container.

7. Apparatus according to claim 6, characterized in that said container (20) is provided with at least a rotating shaft (21) carrying a plurality of stirring blades or  
15       paddles (22) applied to said shaft by means of appropriate arms, and appropriately provided with driving means.

8. Apparatus according to claim 7, characterized in that said means for blowing in and continuously circulating said flow of inert gas comprise:

20       - at least an immission opening (24) adapted to diffuse said inert gas within the mass of said thermoplastic material in said container,

- at least an exhaust opening (26) for letting out said inert gas blown into said container, said exhaust opening being preferably arranged on the opposite side with respect to said gas immission opening.

25

9. Apparatus according to any of the preceding claims 6 to 8, characterized in that it is adapted to directly discharge, via an appropriate conduit (28), the pelletized material contained in said container into the feeding hopper (27) of an extruder.

30       10. Apparatus according to claim 9, characterized in that said conduit (28) and/or said hopper (27) have an air-tight construction sealing them against the outside atmosphere.

FIG. 1

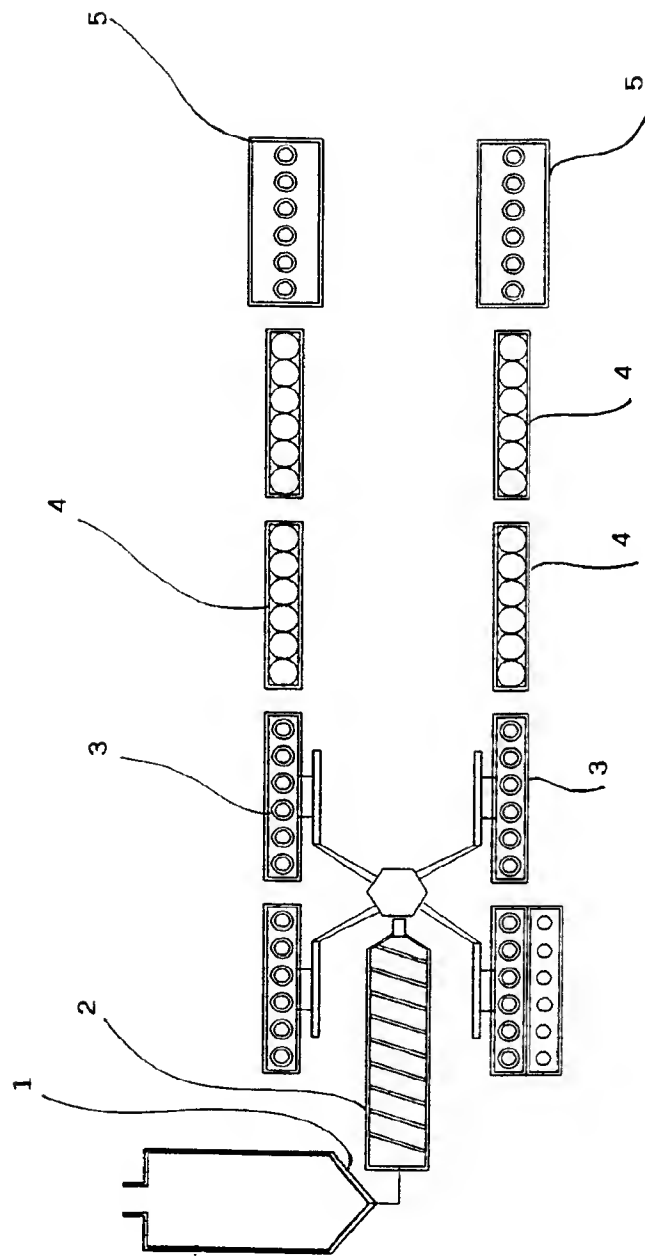


FIG. 2

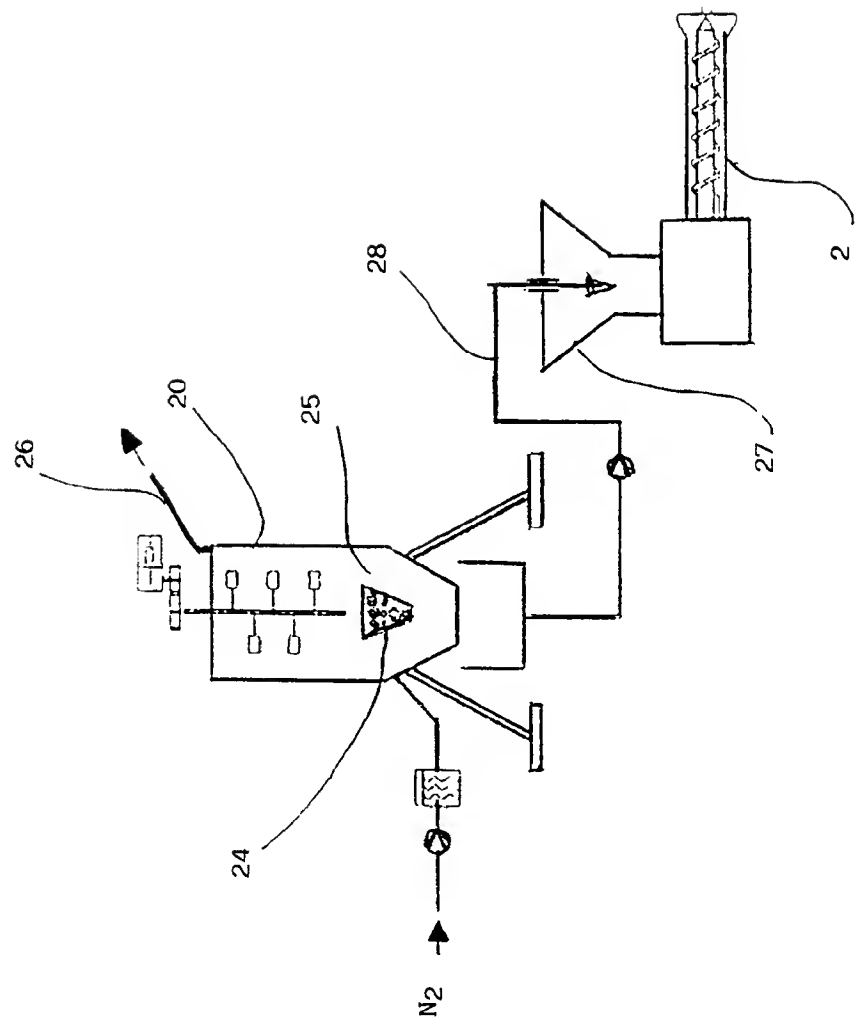


FIG. 3

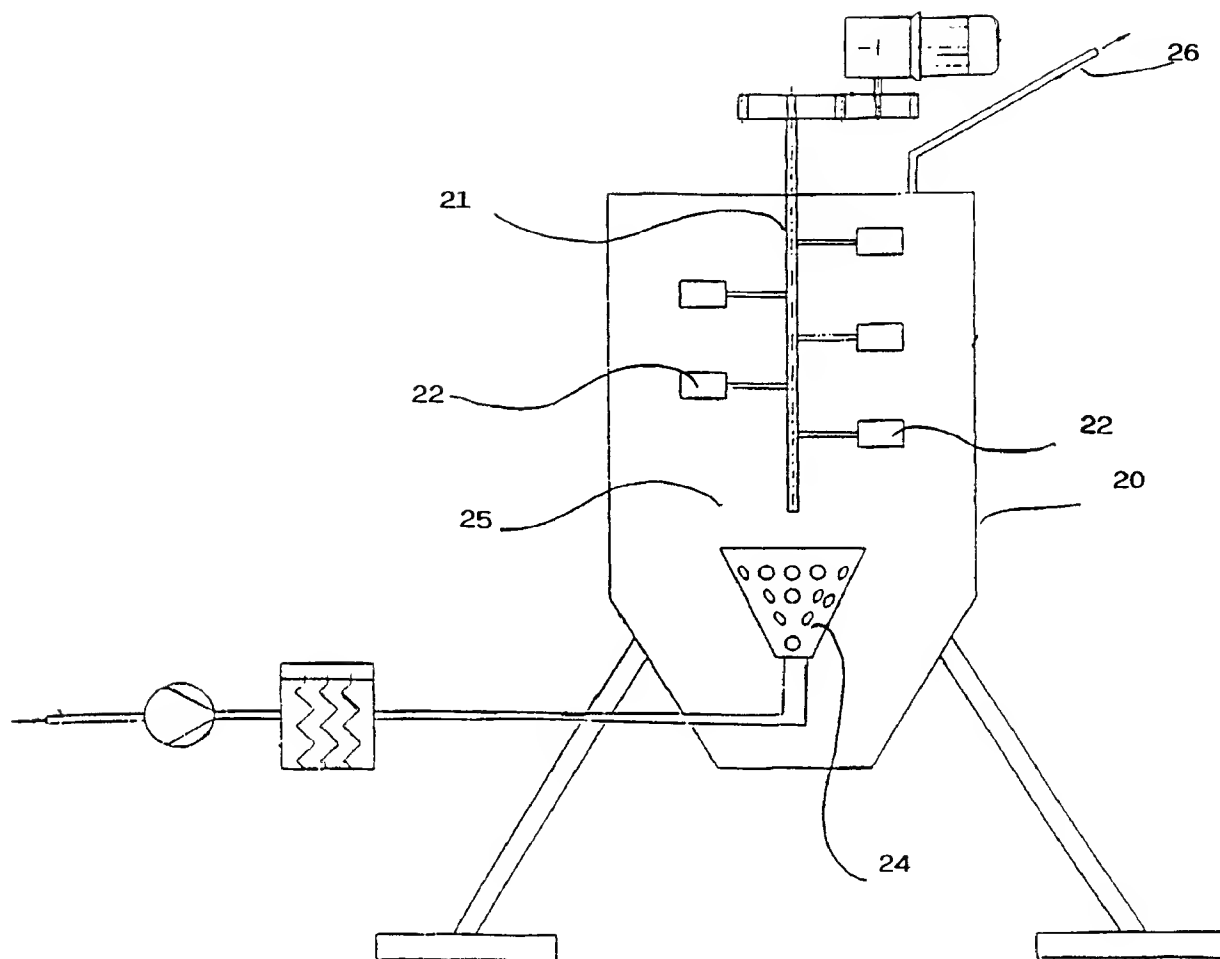
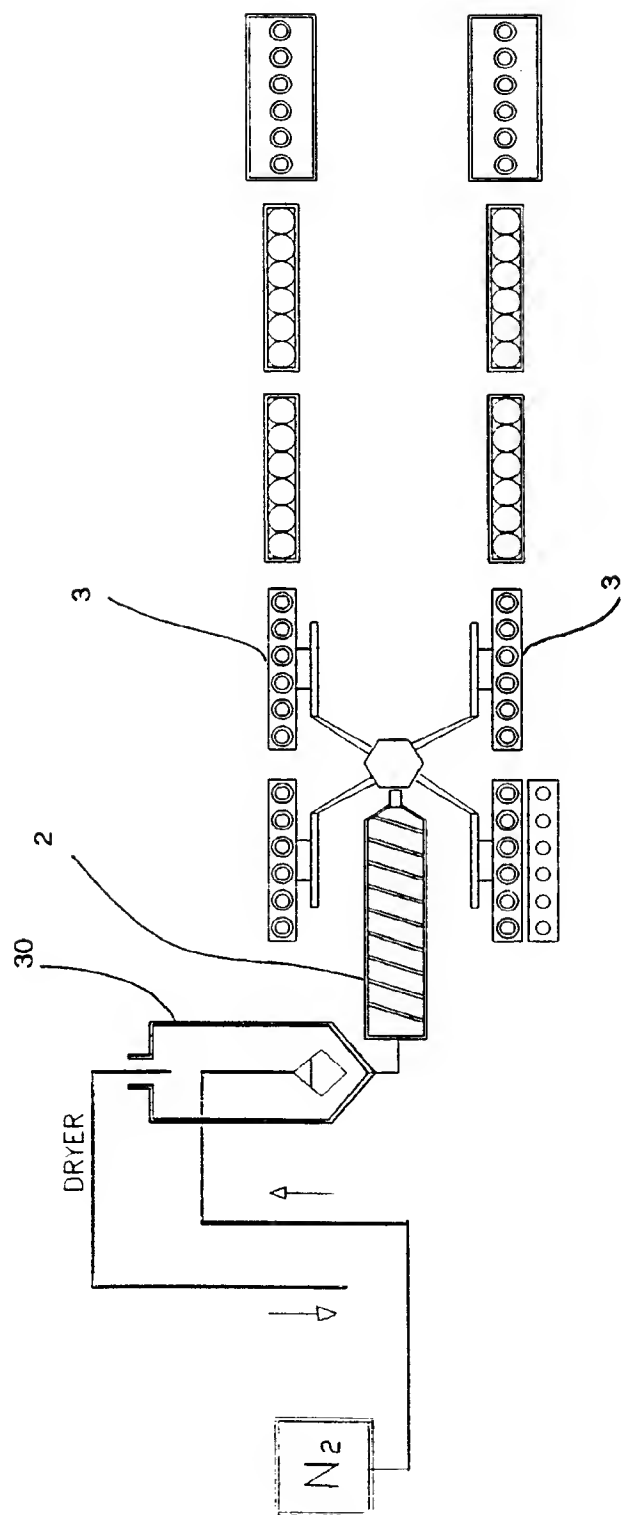




FIG. 4



# INTERNATIONAL SEARCH REPORT

Inter      nal Application No  
PCT/EP 00/01164

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7    B29B13/02    B29B13/06    B29B9/16    B29C49/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7    B29B    B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 333 329 A (PERMIAN) 20 September 1989 (1989-09-20) column 1, line 1-11,30-37; figures 1,2 column 3, line 44-55 column 9, line 22-34; claim 7 ---	1-10
X	GB 1 223 646 A (ALLIED CHEMICAL) 3 March 1971 (1971-03-03) page 1; claims 1,6; figure 1 ---	1-10
X	US 3 661 330 A (ASADA YOSHIHARU ET AL) 9 May 1972 (1972-05-09) column 3, line 2-13; figures 1-3 column 4, line 21-24 ---	1-10
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

10 May 2000

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/01164

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 14 54 843 A (N.V.O.) 6 March 1969 (1969-03-06) page 1, paragraph 2 page 4, paragraph 4; claims 1,2; table 1 ----	1-10
X	EP 0 864 409 A (HOECHST TREVIRA GMBH & CO KG) 16 September 1998 (1998-09-16) column 1, line 53 -column 3, line 8; figure 1 column 4, line 44 -column 5, line 43; claims 6,8,11 ----	1-5
X	US 3 969 314 A (GRIGULL HANS) 13 July 1976 (1976-07-13) column 3, line 4-10; figure 2 ----	1,4,6-10
A	DE 12 20 116 B (ANKERWERK) 30 June 1966 (1966-06-30) column 1, line 34-47 ----	1-10
A	WO 89 07042 A (EREMA) 10 August 1989 (1989-08-10) page 1 ----	1-10
A	US 3 597 850 A (JENKINS JOHN W) 10 August 1971 (1971-08-10) figures 1-5 -----	1-10

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/01164

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0333329	A	20-09-1989	US 4839969 A AU 3074689 A CN 1037207 A,B JP 2004501 A KR 9202380 B US 4974336 A	20-06-1989 31-08-1989 15-11-1989 09-01-1990 23-03-1992 04-12-1990
GB 1223646	A	03-03-1971	US 3495341 A	17-02-1970
US 3661330	A	09-05-1972	JP 51025377 B DE 1779521 A GB 1242023 A NL 6812055 A US 3547890 A	30-07-1976 02-12-1971 11-08-1971 25-02-1969 15-12-1970
DE 1454843	A	06-03-1969	LU 42016 A	07-09-1962
EP 0864409	A	16-09-1998	DE 19709517 A CN 1199061 A JP 10253257 A	17-09-1998 18-11-1998 25-09-1998
US 3969314	A	13-07-1976	DE 2334189 A BE 817324 A CH 568832 A FR 2235775 A IT 1015535 B JP 50039348 A SE 7408856 A	23-01-1975 06-01-1975 14-11-1975 31-01-1975 20-05-1977 11-04-1975 07-01-1975
DE 1220116	B		NONE	
WO 8907042	A	10-08-1989	AT 76350 T BR 8907227 A EP 0390873 A JP 7049201 B JP 3503144 T	15-06-1992 05-03-1991 10-10-1990 31-05-1995 18-07-1991
US 3597850	A	10-08-1971	NONE	